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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
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A process for the preparation of an alkyl alkenoate

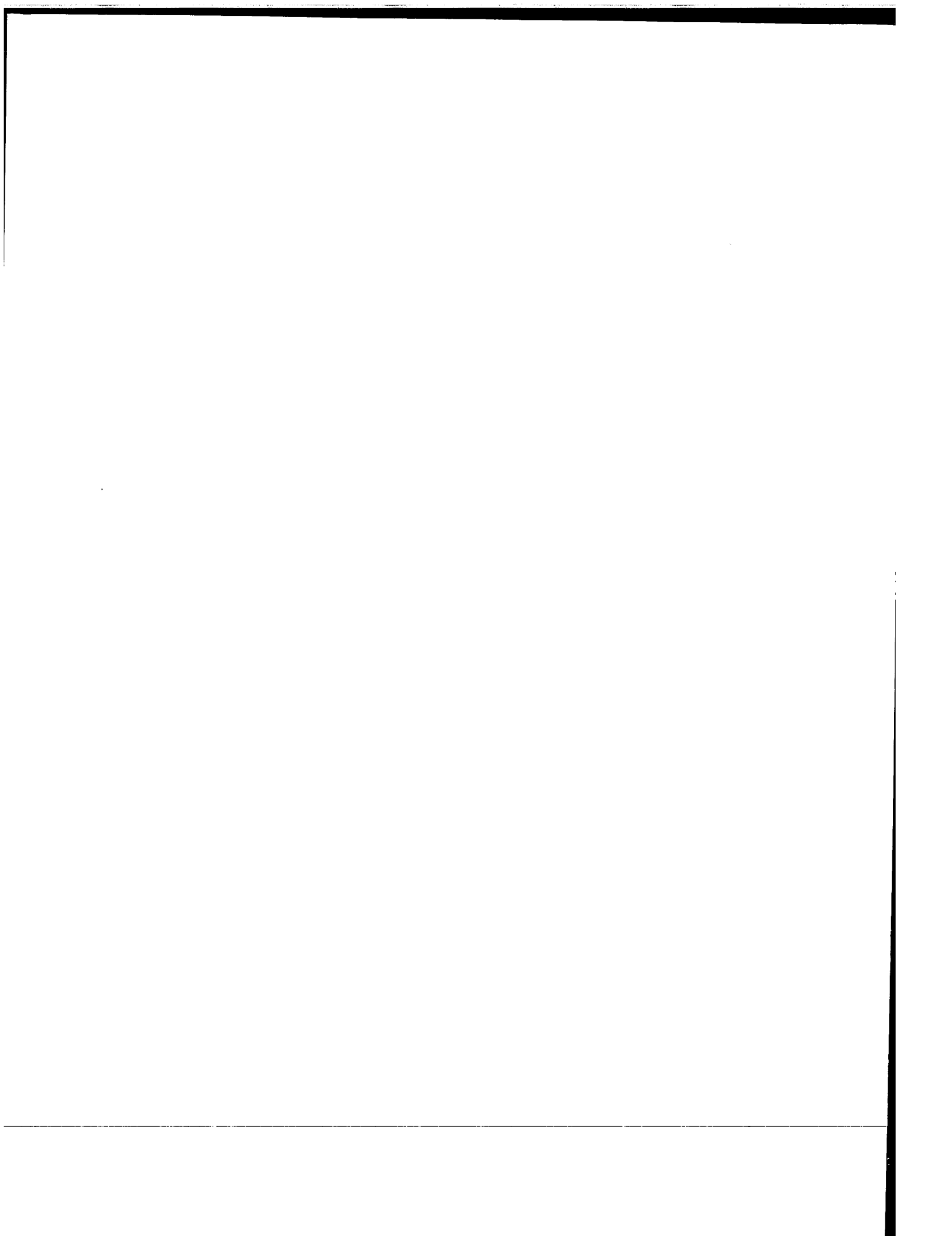
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A PROCESS FOR THE PREPARATION OF AN ALKYL ALKENOATE

Field of the Invention

The present invention relates to process for the preparation of an alkyl alkenoate.

Background of the Invention

5 Pentenoic acid and its esters, can be converted into caprolactam or adipic acid, which are both important nylon precursors. It is known to prepare pentenoic acid or its esters via carbonylation of butadiene. In EP 738 701 for example, a process for the preparation of 3-pentenoic acid is disclosed. Butadiene is
10 hydroxycarbonylated by reacting it with carbon monoxide and water in the presence of an iridium catalyst and an iodide or bromide promoter. In EP 728 733 and EP 728 732, a carbonylation process for the preparation of methyl pentenoate is disclosed, wherein butadiene is reacted
15 with carbon monoxide and methanol in the presence of a carbonylation catalyst system comprising palladium, a carboxylic acid and a phosphine ligand.

Alternatively, alkyl pentenoates can be prepared by contacting an alkoxy-butene and carbon monoxide in the
20 presence of a carbonylation catalyst. In WO 96/29300, for example, a process for the preparation of methyl pentenoate is described wherein a mixture of 3-methoxy-1-butene and 1-methoxy-2-butene is carbonylated with carbon monoxide in the presence of a catalyst. In US 6,175,036,
25 a similar process is disclosed.

In EP 395 038, a process is disclosed for the preparation of adipic acid, wherein a lactone is reacted

with carbon monoxide and water in the presence of a homogeneous rhodium catalyst and an iodide or bromide promoter.

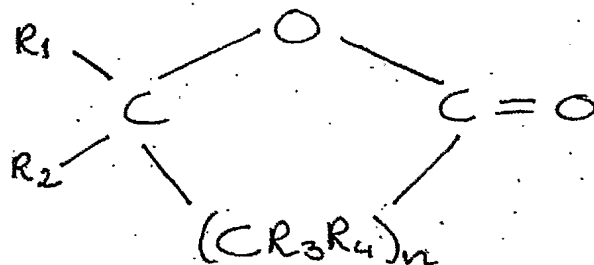
The above-mentioned carbonylation processes have several disadvantages. Carbonylation requires catalysts comprising expensive noble metals and expensive ligands. Since the catalysts are homogeneous catalysts, it is difficult to recover all of the noble metals and the ligands from the reaction products. Moreover, the processes require the use of carbon monoxide, which is a toxic compound.

Therefore, there is a need in the art for an alternative process for the preparation of pentenoates.

Summary of the Invention

An alternative route for the preparation of alkyl alkenoates has been found. It has been found that alkyl alkenoates can be prepared from a lactone as starting material by reacting the lactone and an alkyl alcohol with each other under distillative transesterification conditions in the presence of a strong acid catalyst.

Accordingly, the present invention relates to a process for the preparation of an alkyl alkenoate, wherein a lactone of the general formula



wherein n is 1, 2 or 3, R₁ is a C1-C4 alkyl group, and R₂, R₃ and R₄ are a H atom or a C1-C4 alkyl group,

is reacted with a C1-C4 alkyl alcohol in the presence of a strong acid catalyst at transesterification conditions in a reaction zone to form the alkyl alkenoate, wherein alkyl alkenoate and alcohol are continuously removed from the reaction zone by distillation.

The process according to the invention has several advantages as compared to the known carbonylation processes. In the process according to the invention simpler, cheaper catalysts can be used. No high pressure is needed for the process. The process is highly selective and the reactant lactone can be obtained from renewable feedstocks such as biomass.

Brief Description of the Drawings

Two embodiments of the invention are described in detail and by way of example with reference to drawings 1 and 2.

Figure 1 schematically depicts a flow diagram of a first embodiment, using a distillation column with an homogeneous catalyst.

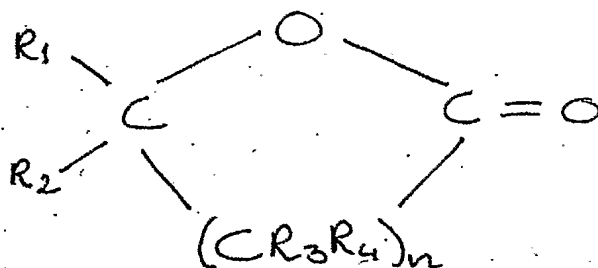
Figure 2 schematically depicts a flow diagram of a second embodiment, using a distillation column with an heterogeneous catalyst.

Detailed Description of the Invention

In the process according to the invention, a lactone and an alcohol are reacted with each other to form an alkyl alkenoate in the presence of a strong acid catalyst under reactive distillation conditions.

The lactone may be any 4-, 5-, or 6-membered ring lactone, wherein the ring carbon atom that is next to the ring-closing oxygen atom is substituted with a C1-C4 alkyl group. The other ring carbon atoms may be unsubstituted or substituted with C1-C4 alkyl groups.

The lactone is of the general formula



wherein n is 1, 2 or 3, R₁ is a C1-C4 alkyl group and R₂, R₃ and R₄ are a H atom or a C1-C4 alkyl group.

The ring carbon atom that is next to the ring-closing oxygen atom is preferably substituted with a methyl or ethyl group, more preferably with a methyl group. Thus, R₁ is preferably methyl or ethyl, more preferably methyl. R₂ is preferably a hydrogen atom.

The other ring carbon atoms are preferably unsubstituted. Therefore, both R₃ and R₄ are preferably a hydrogen atom for each carbon atom. If the other ring carbon atoms are substituted, the R₃ or R₄ groups may differ for each carbon atom.

The lactone is preferably a 5-membered ring lactone. Thus, n is preferably 2.

Examples of suitable lactones are gamma valerolactone, delta caprolactone or gamma caprolactone. A particularly suitable lactone is gamma valerolactone. If the lactone is gamma valerolactone, the alkyl alkenoate that is formed is alkyl pentenoate. Under the acid conditions of the process of the invention, a mixture of 2-, 3-, and 4-pentenoate will be formed with the 2- and 3-pentenoate both in the cis and the trans configuration.

The lactone and the alcohol are reacted with each other at distillative transesterification conditions in the presence of a strong acid catalyst. Alkyl alkenoate

is formed by the transesterification reaction and the alkyl alkenoate and alcohol are continuously removed from the reaction mixture by distillation.

5 It will be appreciated that the temperature of the reaction zone is such that the alkyl pentenoate can be distilled from the reaction zone. Therefore, the temperature is above the boiling temperate of the lowest-boiling azeotrope containing the alkyl pentenoate and below the boiling temperature of the lactone. The exact
10 temperature will thus depend on the reactants used and on the operating pressure in the reaction zone. Typically, the temperature will be in the range of from 100 to 300 °C, preferably in the range of from 150 to 250 °C.

15 The process may be operated at any suitable pressure. It is an advantage of the process according to the invention that no high pressure conditions are needed. Preferably, the pressure is in the range of from 0.01 to 10 bar (absolute), more preferably of
20 from 0.1 to 5 bar (absolute), even more preferably the pressure is ambient pressure.

It will be appreciated that a difference in boiling temperature between the lactone and the alkyl alkenoate is needed in the process according to the invention. In
25 order to have such a difference in boiling point, the alcohol with which the lactone is reacted is a C1-C4 alkyl alcohol, preferably methanol or ethanol, more preferably methanol.

30 The process according to the invention may be catalysed by an homogeneous or an heterogeneous strongly acidic catalyst. Thus, the catalyst may be a liquid or a solid strong acid. Preferred liquid strong acids are sulphuric acid or p-toluene sulphonic acid (pTSA).

Examples of suitable strongly acidic solids are ion-exchange resins and strongly acidic mixed oxides such as acidic crystalline silica-alumina (zeolites). Preferred strongly acidic solid catalysts are ion-exchange resins, acidic ZSM-5 zeolite and acidic beta zeolite.

The process according to the invention may be operated as a batch, semi-batch or continuous process. Preferably, the process is operated as a continuous process wherein lactone and alcohol are continuously supplied to the reaction zone and alkyl alkenoate, alcohol, and water are continuously removed from the reaction zone by distillation. More preferably, the continuous process is performed in a distillation column.

It is known in the art how to design a distillation column for reactive distillation purposes. Reference is for example made to G. Ertl, H. Knözinger, J. Weitkamp (Eds), Handbook of Heterogeneous Catalysis, Volume 3, 1997, VCH, pp 1479-1487. It will be appreciated that a design for a reactive distillation column for an homogeneous catalytic reaction is different from one for an heterogeneous catalytic reaction. For illustrative purposes, two embodiments of the process of the invention are shown in Figures 1 and 2, one for homogeneous catalysis (Figure 1) and one for heterogeneous catalysis (Figure 2).

If the process is performed in a distillation column and the catalyst is a solid catalyst (heterogeneous catalysis), the distillation column comprises a reaction zone containing the solid catalyst. This reaction zone has both a reaction and a distillation function. Suitable solid catalyst structures for such a double function reaction zone are known in the art, for example from US 4,443,559. The distillation column preferably

comprises additional distillation zones above and/or below the reaction zone. These additional distillation zones each comprise at least one theoretical fractionation stage in the form of conventional distillation trays or inert packing.

The homogeneous catalyst is preferably present in a concentration in the range of from 0.01 to 20 % by weight based on the weight of lactone in the reaction zone, more preferably of from 0.1 to 10% by weight. If the catalyst is an heterogeneous catalyst and the process is performed as a batch or semi-batch process, the preferred catalyst concentrations are as described above for the homogeneous catalyst.

It will be appreciated that in the case of an heterogeneous catalyst in a reactive distillation column, it is more appropriate to express the catalyst concentration in terms of a weight hourly velocity of the lactone. Preferably, the lactone weight hourly velocity is in the range of from 0.1 to 10 kg lactone per kg catalyst per hour, more preferably of from 0.5 to 5 kg/kg/h.

Detailed description of the drawings

Figure 1 shows a distillation column 1, which has a stripping section 2 and a rectifying section 3, each section comprising at least one theoretical fractionation stage. Before starting normal operation of the column, a strong liquid acid catalyst, e.g. sulphuric acid, is introduced into column 1. During normal operation of distillation column 1, gamma valerolactone, optionally with some acid catalyst, is continuously introduced in column 1 via line 4 at a point between stripping section 2 and rectifying section 3. Methanol is continuously introduced into column 1 below stripping

section 2, via line 5. The methanol may be introduced in column 1 as a vapour or may be vaporised upon entering column 1. A liquid bottoms stream comprising gamma valerolactone and the acid catalyst is withdrawn from distillation column 1 via line 6. Part of the bottoms stream is vaporised in reboiler 7 and re-introduced in column 1 via line 8. Part of the liquid bottoms stream is recycled to feed line 4 via line 9 and re-introduced in column 1 with the fresh lactone. A small part of the bottoms stream may be purged via line 10. A gaseous overhead stream comprising methyl pentenoate, water and methanol is withdrawn from column 1 via line 11 and condensed in condenser 12. Part of the condensed stream is withdrawn as product stream via line 13. The remainder is reintroduced in column 1 just above rectifying section 3, via line 14.

It will be appreciated that the reaction zone is that part of the column where the acid catalyst and the reactants are present, i.e. the part of the column between the methanol inlet and the inlet of the partly condensed bottoms stream. The height of the inlet of the partly condensed bottoms stream thus determines the length of the reaction zone.

In Figure 2 is shown a distillation column 20, which has a reaction zone 21 containing the solid acidic catalyst, a stripping section 22 below the catalyst bed and a rectifying section 23 above the catalyst bed. The stripping and rectifying sections 22, 23 and the reaction zone 21 each comprise at least one theoretical fractionation stage. Gamma valerolactone is introduced into column 20 above reaction zone 21 via line 24 and methanol is introduced into column 20 below reaction zone 21 via line 25. A liquid bottoms stream comprising gamma

valerolactone is withdrawn from distillation column 20 via line 26. Part of the bottoms stream is vaporised in reboiler 27 and re-introduced in column 20 via line 28. Part of the liquid bottoms stream is recycled to feed line 24 via line 29 and re-introduced in column 20 with the fresh lactone. A small part of the bottoms stream may be purged via line 30. A gaseous overhead stream comprising methyl pentenoate, water and methanol is withdrawn from column 20 via line 31 and condensed in condenser 32. Part of the condensed stream is withdrawn as product stream via line 32. The remainder is reintroduced in column 20 just above rectifying section 23, via line 34.

In the embodiments of both Figures 1 and 2, methyl pentenoate and/or methanol may be separated from the product stream comprising methyl pentenoate, methanol and water by means known in the art (not shown), such as fractionation, extraction, liquid/liquid separation, or a combination thereof. The separated methanol may then be recycled to line 5 or line 25.

Examples

The invention is now illustrated by means of the following non-limitative examples.

EXAMPLES 1-14

A 250 ml three-neck glass flask was provided with a rectification column with a length of 20 cm, which was filled with metal barrel seeds and was connected to a water cooler and collection flask. The three-neck flask was loaded with 80 g lactone and acid catalyst. The flask was heated to 190 °C and alcohol was continuously fed to the flask. The volatile compounds, i.e. alkyl pentenoate, alcohol, and water, were stripped from the reaction

mixture by a flow of nitrogen of 0.6 litre per hour. The distillate product was collected and analysed by GLC. Different experiments were carried out using different catalysts, alcohols and lactones. All experiments were performed at ambient pressure.

In EXAMPLE 5, 60 g gamma valerolactone, 30 g methanol, and 2 g pTSA were loaded in a 300 ml steel autoclave, purged with nitrogen and pressurised to 1 bar (absolute) with nitrogen. The autoclave was heated to 200°C under autogeneous pressure. After 26 hours, the autoclave was cooled down and the liquid product analysed by GLC. In this experiment, methanol and methyl pentenoate were thus not distilled from the reaction zone.

The Table below shows the reactants, catalyst, alcohol feed rate, duration and product yield for each experiment. Examples 1-4, 6-9, and 13 are examples according to the invention; examples 5, 10-12, and 14 are comparative examples.

The product yield as shown in the Table is the yield calculated from the amount of pentenoate found in the distillate. The amount of pentenoate that is formed might be somewhat higher, since some pentenoate might have remained in the reaction flask.

The liquid reaction mixture obtained after the experiment in EXAMPLE 5 (no distillation) contained 50 g unconverted gamma valerolactone, 2.5 g methyl pentenoate, 2.4 g of heavy products, methanol and a significant amount of dimethyl ether.

Table Results of examples 1-14

example	lactone ¹	alcohol ²	catalyst ³	catalyst conc. (mg/g lactone)	feed rate alcohol (mg/g lactone.h)	time (h)	mole% product
homogeneous strong acid catalysts							
1	gVL	MeOH	H ₂ SO ₄	20	76	6.5	56
2	gVL	MeOH	H ₂ SO ₄	16	62	6	33
3	gVL	MeOH	pTSA	62	73	6	37
4	gVL	MeOH	pTSA	31	74	6	23
5 (comparison) no distillation	gVL	MeOH	pTSA	33	0	25 26	91 3.7
heterogeneous strong acid catalysts							
6	gVL	MeOH	H-β 200	53	77	6	25
7	gVL	MeOH	H-β 22	56	77	6	26
8	gVL	MeOH	H-ZSM-5	42	73	6.2	29
9	gVL	MeOH	Nafion NR-50	29	74	5.3	34

Table continued

heterogeneous medium and weak acid catalysts							
10 (comparison)	gVL	MeOH	ASA	28	82	5.5	1.7
11 (comparison)	gVL	MeOH	γ -Al ₂ O ₃	50	74	6.5	< 0.1
12 (comparison)	gVL	MeOH	La/Al ₂ O ₃	66	95	5.5	< 0.1
Different alcohol							
13	gVL	EtOH	pTSA	32	69	27	22.5
Different lactone							
14 (comparison)	gBL	MeOH	pTSA	40	32	5.7	-

¹ gVL: gamma valerolactone; gBL: gamma butyrolactone.

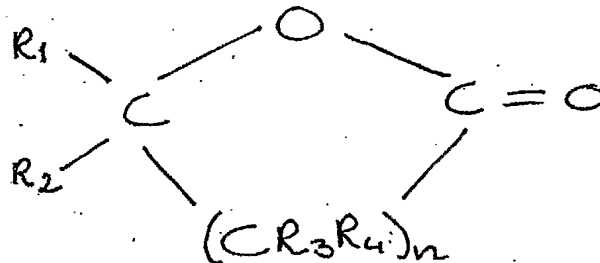
² MeOH: methanol; EtOH: ethanol.

³ H- β 22, H- β 200: acidic beta zeolite with a silica-to-alumina molar ratio of 22 and 200, respectively; H-ZSM-5: acidic ZSM-5 zeolite; Nafion NR-50: commercially available ion-exchange resin (ex. Dupont); ASA: amorphous silica-alumina; La/Al₂O₃: 16% by weight La on alumina.



C L A I M S

1. A process for the preparation of an alkyl alkenoate, wherein a lactone of the general formula



wherein n is 1, 2 or 3, R_1 is a C1-C4 alkyl group, and R_2 , R_3 and R_4 are a H atom or a C1-C4 alkyl group,

is reacted with a C1-C4 alkyl alcohol in the presence of a strong acid catalyst at transesterification conditions in a reaction zone to form the alkyl alkenoate, wherein alkyl alkenoate and alcohol are continuously removed from the reaction zone by distillation.

2. A process according to claim 1, wherein R_1 is an ethyl or a methyl group, preferably a methyl group.

3. A process according to claim 1 or 2, wherein R_2 is a hydrogen atom.

4. A process according to any one of the preceding claims, wherein both R_3 and R_4 are a hydrogen atom.

5. A process according to any one of the preceding claims, wherein n is 2.

6. A process according to any one of the preceding claims, wherein the lactone is gamma valerolactone and the alkyl alkenoate is alkyl pentenoate.

7. A process according to any one of the preceding claims, wherein the temperature of the reaction zone is

maintained in the range of from 100 to 300 °C, preferably of from 150 to 250 °C.

5 8. A process according to any one of the preceding claims, wherein the pressure in the reaction zone is in the range of from 0.01 to 10 bar (absolute), more preferably of from 0.1 to 5 bar (absolute), even more preferably ambient pressure.

10 9. A process according to any one of the preceding claims, wherein the alkyl alcohol is methanol or ethanol, preferably methanol.

10. A process according to any one of the preceding claims, wherein the catalyst is a strong liquid acid, preferably sulphuric acid or p-toluene sulphonic acid.

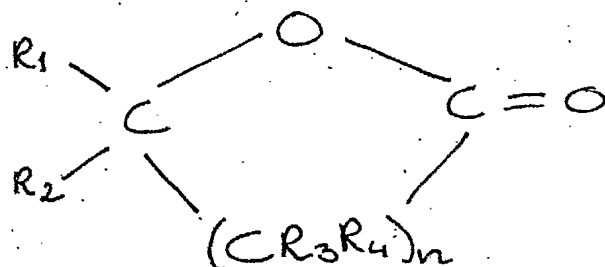
15 11. A process according to any one of claims 1 to 9, wherein the catalyst is a strongly acidic solid, preferably an ion-exchange resin or acidic ZSM-5 or beta zeolite.



A B S T R A C T

A PROCESS FOR THE PREPARATION OF AN ALKYL ALKENOATE

A process for the preparation of an alkyl alkenoate, wherein a lactone of the general formula



wherein n is 1, 2 or 3, R_1 is a C1-C4 alkyl group, and R_2 , R_3 and R_4 are a H atom or a C1-C4 alkyl group,

is reacted with a C1-C4 alkyl alcohol in the presence of a strong acid catalyst at transesterification conditions in a reaction zone to form the alkyl alkenoate, wherein alkyl alkenoate and alcohol are continuously removed from the reaction zone by distillation.

(Figure 1)

Fig.1.

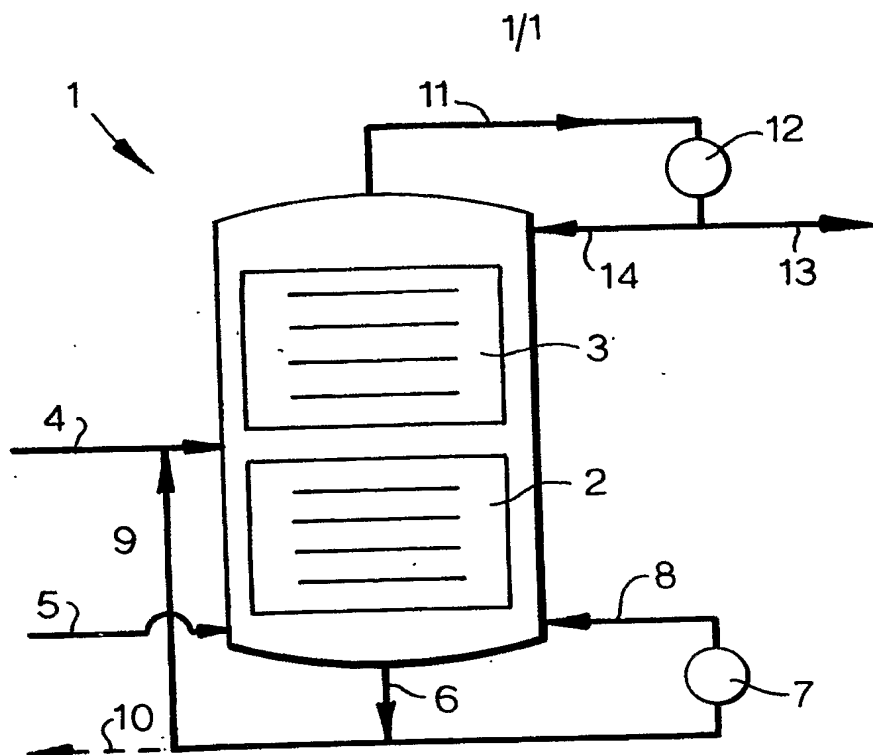


Fig.2.

